

$$K_{\perp} = 4\pi\epsilon\kappa_1\kappa_2 \cdot h \frac{R_1^2 R_2^2}{(R_1 + R_2)^3} \cdot \gamma E_{\parallel} E_{\perp}.$$

The following abbreviations are used:

$$\kappa_i = \frac{\epsilon_i - \epsilon}{\epsilon_i + \epsilon}; \quad c = \kappa_1 \kappa_2; \quad l = \frac{R_1 R_2}{R_1 + R_2}; \quad r = \frac{l}{2R_1};$$

$$s = 1 - r.$$

The coefficients α , β , γ are evaluated by means of the series (22, 23, 24) and the function $I(c, \kappa_2)$ is defined in (31). One finds

$$\alpha = -\frac{R_1 R_2}{2\kappa_2 l^2} \cdot I(c, \kappa_2)$$

$$\beta = -\frac{R_1 R_2}{2\kappa_2 l^2} \cdot I(c, -\kappa_2) = -\alpha(-\kappa_1, -\kappa_2)$$

$$\gamma = F_c(1).$$

The use of a programmable calculator enables one to compute the coefficients in a minute, provided that $|\kappa_1|$ and $|\kappa_2|$ lie below 0.95. For larger values, the time of computation increases rapidly.

The Limiting Case of equal Cylinder radii $R_1 = R_2$

The formulae simplify considerably in this case. We quote them here, but skip the explicit calculations. Although these may be derived from the general formulae given above as a special case, it is far simpler to start with an integration over $\zeta = 0$, as described in part I.

For $R_1 = R_2$, one obtains

$$\alpha = -\frac{1}{2}F_c(1) - \frac{4}{3}(\kappa_1 + \kappa_2)D_c\left(\frac{3}{2}\right) - 4cH_c(2)$$

$$\beta = \frac{1}{2}F_c(1) - \frac{4}{3}(\kappa_1 + \kappa_2)D_c\left(\frac{3}{2}\right) + 4cH_c(2) \quad (36, \text{II})$$

$$\gamma = F_c(1).$$

In the above the definition is used

$$D_c(a) = Z_{1,2} = \frac{1}{2} \sum_{n=0}^{\infty} \frac{(n+1)(n+2)}{(n+3-a)^2} c^n. \quad (37, \text{II})$$

By repeated use of the functional equation given under the definition (21), one gets the general relation

$$\begin{aligned} (k+1) \cdot Z_{k,k+1}(c, a) &= \frac{1}{1-c} + (a-1) \cdot Z_{k,k}(c, a-1) \\ &+ (a-2) \cdot Z_{k-1,k-1}(c, a-2) + \dots \\ &+ (a-k-1) \cdot Z_{0,0}(c, a-k-1) \\ (k &= 0, 1, \dots) \end{aligned} \quad (38, \text{II})$$

(38) enables us to transform the series $D_c(a)$ and $H_c(a)$ into those that converge better in the neighbourhood of 1. With a programmable calculator, the coefficients α , β , γ can thus be determined with great accuracy for values of $|c|$ up to 0.99 in a matter of minutes.

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Solubility and Diffusion of Chlorine in Silica Glass

Wilhelm Hermann, Hans Rau, and Joachim Ungelenk

Philips GmbH Forschungslaboratorium Aachen, D-5100 Aachen, Germany

Diffusion / Glasses

Chlorine diffusion profiles in silica glass have been studied by SEM techniques. From the results the diffusion coefficient D ($\log_{10}(D \cdot \text{cm}^{-2} \text{ s}) = -11080 \text{ K}/T - 3.498$), the equilibrium solubility of Cl in silica glass (0.25 or 0.32 weight per cent at 1 bar Cl_2 pressure and 1438 K or 1970 K), and the pressure dependence of the solubility were derived. The latter is proportional to the fourth root of the Cl_2 pressure. There are no detectable differences in the behaviour of chlorine in silica made by the PCVD method (plasma activated chemical vapour deposition) or in commercially produced silica (HERALUX, wave guide quality), but the chlorine concentration is much higher in PCVD silica than expected from the small chlorine pressures present during deposition.

Introduction

Very little is known of the solubility and the diffusion of chlorine in silica. In the "Handbook of Glass Data" [1] nothing is said on this subject. Some information is given

by Greeuw and Hasper [2] who implanted chlorine in SiO_2 layers grown on silicon. They found that chlorine becomes mobile in SiO_2 above 1000 K and derived a tentative diffusion coefficient. Hanafusa and Tajima [3] measured

chlorine concentration profiles in optical fibres based on SiO_2 .

During deposition of (doped) silica layers in a silica tube for the preparation of optical fibres using the PCVD method [4] significant amounts of chlorine are incorporated (0.3–1.1 weight per cent). Since this effect is of rather great significance for the PCVD process we decided to determine the solubility of chlorine in silica as a function of Cl_2 pressure and temperature and the diffusion coefficient as a function of temperature.

Experimental

Samples Prepared by the PCVD Method

A mixture of oxygen ($2.2 \cdot 10^{-4}$ mol/s) and silicon tetrachloride ($3.7 \cdot 10^{-5}$ mol/s) flowing through a silica tube of 14 mm internal diameter at 10 mbar pressure and 1530 K was activated by a moving non-isothermal plasma generated using a microwave resonator (2.45 GHz, 500 W). Thus, the reaction



took place in the plasma region and the SiO_2 formed was condensed at the wall of the tube to clear thin glass layers. After having deposited about 0.3 mm in thickness the reaction was stopped and the tube cooled to room temperature. Slices of the tube taken perpendicular to the axis were annealed at different temperatures for a sufficiently long time to allow the chlorine incorporated in the deposited layers to diffuse into the original silica tube which was known to be free of chlorine at the beginning (HERALUX, wave guide quality). The slices were embedded in suitable plastic and polished to optical quality. After vapour deposition of carbon the chlorine concentration profiles of the samples were measured with a scanning electron microscope (SEM) (runs 1–3).

Annealing of Silica Ampoules or Tubes with Chlorine Gas

Known amounts of chlorine were condensed into silica ampoules of known volume which were subsequently sealed. Each ampoule also contained a rod of silica glass. The ampoules were then annealed in an electrical furnace. After cooling down and condensing the chlorine gas the ampoules were opened and slices were taken from the ampoule walls, embedded and polished as described above (runs 4–6). The rods were treated in a nuclear reactor with $3.2 \cdot 10^{11}$ neutrons $\text{cm}^{-2} \text{s}^{-1}$ for one hour and the total chlorine diffused into them was calculated from the intensity of its characteristic gamma radiation (runs 8–10).

At 1970 K the treatment with chlorine could only be performed by using a flow of chlorine gas of exactly ambient pressure through

a tube mounted in a suitable furnace because silica is no longer hard at this temperature (run 7).

Scanning Electron Microscope (SEM) Analyses

The experimental conditions in the energy dispersive X-ray analysis carried out in a scanning electron microscope were as follows: 12 keV excitation energy, 200 nm spot size, approx. $2 \cdot 10^{-9}$ A probe current and 15 degree specimen tilt angle. The method was calibrated by analysing the same specimens with wet chemical methods. The profiles were obtained either by point to point measurements or, in order to avoid the influence of small defects in the surface on the results, by analysing a set of parallel line scans perpendicular to the slope of the profile. The propagated 1-sigma statistical error achieved was 9% at chlorine levels of 0.3 weight per cent in silica glass. In analysing a chlorine step profile (composite specimen consisting of a piece of chlorine doped silica glass and a piece of pure silica glass precisely polished and fitted to each other) it has been verified that under the chosen experimental conditions the spatial resolution is better than one micrometer.

Results and Evaluations

Table 1 shows the experimental conditions used and some results derived from them.

Figs. 1–3 show measured chlorine profiles and theoretical curves fitted to them. In type A experiments (PCVD deposited layers in a silica tube) the starting chlorine profile had to be taken into account when calculating the diffusion coefficient, because chlorine had already diffused somewhat during the deposition time. Type B experiments (runs 4 and 7) allowed the solubility in equilibrium with the gas phase to be calculated, since it can be assumed that the innermost surface, which is always in contact with the chlorine atmosphere, should therefore be in equilibrium with it.

Fig. 4 shows the temperature dependence of the diffusion coefficient of chlorine in silica glass (HERALUX w.g. or deposited by the PCVD process). The fitted straight line, showing no difference of the diffusion coefficient in the two different materials, corresponds to

$$\log_{10} (D \cdot \text{cm}^{-2} \text{s}) = -11080 \text{ K}/T - 3.498 \quad (2)$$

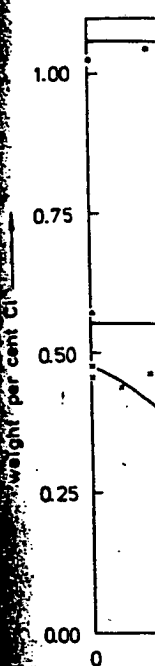
The activation energy of Eq. (2) (212 kJ/mol) is rather similar to that estimated by Greeuw and Hasper [2] (193 kJ/mol), but our diffusion coefficients are about a factor 30 higher at the temperatures used by Greeuw and Hasper. Using the diffusion coefficient and the solubility of run 4 the total amount of chlorine expected to be taken up by the silica rod in the ampoule could be calculated. The expected value (23.4 μg) and that found (23.3 μg) were in good agreement.

Table 1

Experimental conditions and some results derived from them.

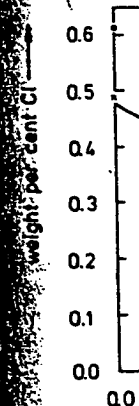
Type: (A) deposited PCVD layers in a tube or (B) elemental chlorine in silica ampoules or tubes. $P(\text{Cl}_2)$: Cl_2 partial pressure during annealing. T : temperature. τ : Annealing time at pressure $P(\text{Cl}_2)$ and temperature T . $S(\text{Cl}_2)$: Equilibrium solubility of chlorine (weight per cent) in HERALUX w.g. at pressure $P(\text{Cl}_2)$ and temperature T . $S_0(\text{Cl}_2)$: Equilibrium solubility of chlorine (weight per cent) at pressure 1 bar and temperature T . $D(\text{Cl}_2)$: Diffusion coefficient. Analysis: either SEM or neutron activation (NA). $W(\text{Cl}_2)$: total weight of chlorine taken up by a silica rod of 2.40 cm^2 surface

Run	Type	$P(\text{Cl}_2)$ bar	T K	τ s	$S(\text{Cl}_2)$ %	$S_0(\text{Cl}_2)$ %	$D(\text{Cl}_2)$ cm^2/s	Analysis	$W(\text{Cl}_2)$ μg
1	A	—	1628	67300	—	—	$4.11 \cdot 10^{-11}$	SEM	—
2	A	—	1748	9720	—	—	$1.69 \cdot 10^{-10}$	SEM	—
3	A	—	1965	2430	—	—	$7.26 \cdot 10^{-10}$	SEM	—
4	B	13.4	1438	104400	0.48	0.25	$6.46 \cdot 10^{-12}$	SEM	—
5	B	5.6	1438	104400	—	—	—	SEM	—
6	B	2.0	1438	104400	—	—	—	SEM	—
7	B	0.52	1970	2700	0.27	0.32	—	SEM	—
8	B	13.4	1438	104400	—	—	—	NA	23.3
9	B	5.6	1438	104400	—	—	—	NA	21.4
10	B	2.0	1438	104400	—	—	—	NA	14.9



Chlorine diffusion profiles (Table 1) and c

O: $T =$



Chlorine diffusion profiles (Table 1) and c

Runs 8–10: to be calculated by 1/4 (Fig. 5). — 6 given in Fig. 4. Pressure dependence of the diffusion coefficient is neglected, which it is not, but the effect is small.

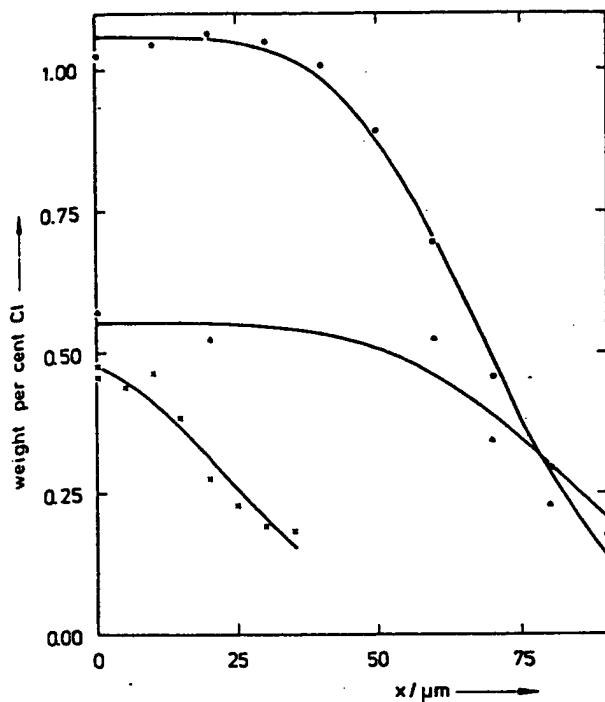


Fig. 1

Chlorine diffusion profiles measured (symbols, runs 1-3, see Table 1) and calculated (solid lines fitted to the experimental points).

○: $T = 1965$ K; ×: $T = 1748$ K; ▲: $T = 1628$ K

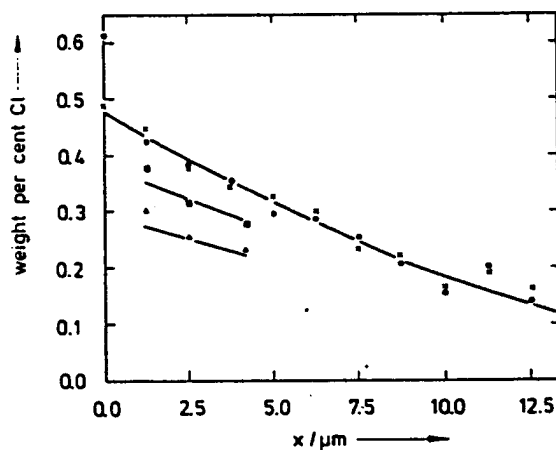


Fig. 2

Chlorine diffusion profiles measured (symbols, runs 4-6, Table 1).
●, ×: $P(\text{Cl}_2) = 13.4$ bar; ■: $P(\text{Cl}_2) = 5.6$ bar; ▲: $P(\text{Cl}_2) = 2.0$ bar. The solid line at 13.4 bar (●, ×) is fitted to the experimental points and the lines at 5.6 bar (■) and 2.0 bar (▲) calculated from the first curve using the pressure dependence

Runs 8-10 allow the Cl_2 pressure dependence of the solubility to be calculated. This is approximately proportional to the power of 1.4 (Fig. 5). This dependence is in good agreement with runs 4-6 given in Fig. 2, where the calculated curves according to that Cl_2 pressure dependence are shown as solid lines. Such a Cl_2 pressure dependence is rather unexpected. It means that each Cl_2 molecule generates four independent centres in the glass matrix in which it is dissolved. Two centres might be the chlorine atoms themselves, but the nature of the two additional centres Z is not

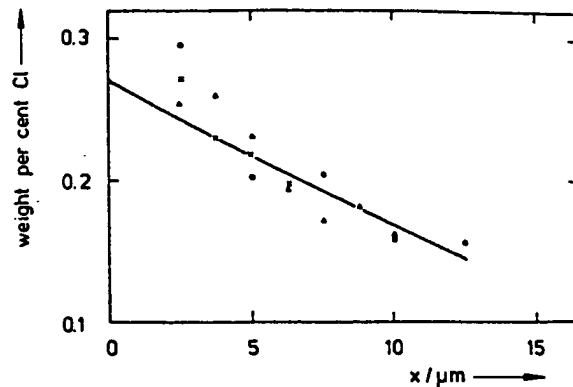


Fig. 3

Chlorine diffusion profile measured (symbols, run 7, see Table 1). The solid line has been fitted to the points using the diffusion coefficient calculated from Eq. (2)

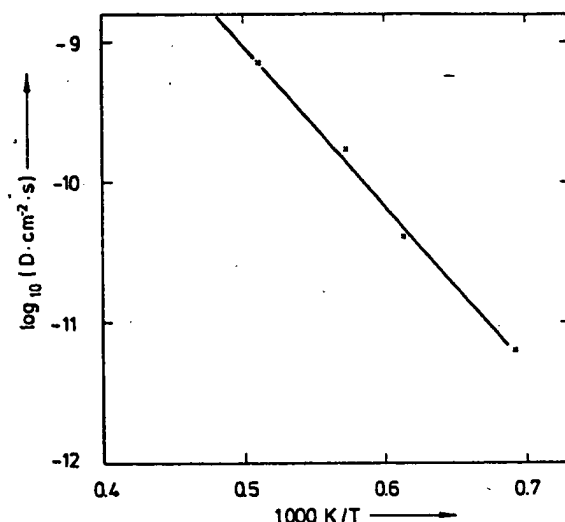


Fig. 4

The diffusion coefficient D of chlorine in silica glass as a function of the temperature T (runs 1-4)

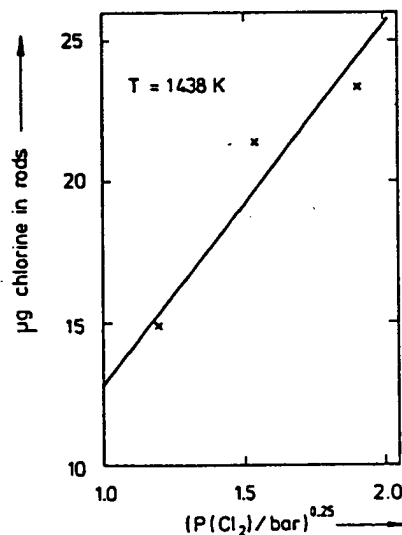


Fig. 5

Cl_2 pressure dependence of the chlorine solubility in silica glass derived from runs 8-10

silica is no longer

lyses

persive X-ray analysis were as follows: $\lambda = 2.2 \times 10^{-9}$ Å. A probe method was called chemical methods. Point measurements effects in the surface scans perpendicular. A statistical error of 1% per cent in silica. A specimen composed of a piece of pure silica (other) it has been conditions the spatial

ed and some results

1 theoretical curves deposited layers in a taken into account. se chlorine had at time. Type B ex- n equilibrium with assumed that the with the chlorine with it. the diffusion coef- g. deposited by with no difference it materials, corre-

(2)

s rather similar to 3 kJ/mol), but our ver at the tempera- diffusion coefficient chlorine expected could be calculated. 3 μg) were in good

aling: T : temperature; $P(\text{Cl}_2)$: pressure; D : diffusion coefficient. Analysis

$W(\text{Cl}_2)$
μg

—
—
—
—
—
—
23.3

clear at the moment. From the reaction between gas phase and glass matrix



a mass action constant

$$K = [\text{Z}]^2 [\text{Cl}]^2 / P(\text{Cl}_2) \quad (4)$$

is derived (brackets mean mole fractions in the glass). With

$$[\text{Z}] = [\text{Cl}] \quad (5)$$

the pressure dependence of the chlorine solubility is

$$S(\text{Cl}_2) = K' P(\text{Cl}_2)^{1/4} \quad (6)$$

Using this relation the solubilities could be calculated at 1 bar Cl_2 pressure (Table 1).

Conclusions

Chlorine diffusion profiles in PCVD deposited silica glass and HERALUX w.g. agree quite well (see Fig. 4). On the other hand, the concentration of chlorine dissolved in PCVD silica is much higher than expected from the small

Cl_2 pressure during deposition (1–3 mbar). This might be a consequence of the very fast plasma reaction. It is well known that plasma reactions may have yields different from those expected for thermodynamic equilibrium [4].

The pressure dependence of the solubility of chlorine in silica glass is rather strange. It should be an interesting investigation to study the nature of the centres formed in silica when chlorine is dissolved in it.

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E 5843

Additivity Rule of the Partial Molal Volume. 2. The Role of the Different Packing Efficiencies around Methylene and Methyl Groups of Normal Alkanes

Y. Yoshimura and M. Nakahara

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

Crystals / Liquids / Molal Volume / Solutions / Thermodynamics

The molecular basis of the additivity rule of the partial molal volume at constant temperature and pressure has been studied for n-alkanes and it is found that the different packing efficiencies around the methylene and methyl groups play an important role in determining the partial molal volume. The different packing efficiencies have been examined in detail in the crystalline phases and the liquid phase. The methyl group is packed looser than the methylene group except for the triclinic crystal phase, and the temperature and pressure dependence of the packing efficiency of the methyl group is larger than that of the methylene group in the liquid state. The different packing efficiencies have been successfully interpreted in a semimicroscopic manner by taking account of the interfacial tension around the hard core of the solute molecule.

1. Introduction

It is impossible to attain the firm and reliable comprehension of the volume profile of the reaction in solution without knowing how the partial molal volume responds to a change in volume of the molecule dissolved in solution. The partial molal volume in solution or the density is one of the fundamental thermodynamic quantities to be determined experimentally, while great efforts are being made to develop liquid theory so as to accomplish the ideal of deriving the entire equation of state for any kind of molecules. Additivity is the simplest form as such a response and very easy to access empirically, and expected to contribute to the understanding of the volume profile of a homologous series of reactions in solution. The first paper [1] in this series has clarified the validity and limitations of the additivity rule of the partial molal volume for n-alkanes over a wide range of temperature and pressure. In the present paper we at-

tempt to elucidate the physical significance of the parameters involved in the additivity rule from the molecular point of view by resorting to some model and crystal systems.

In the previous work on n-alkanes [1] the following facts have been revealed: (i) in both solutions at infinite dilution and neat liquids, the additivity rule of the configurational partial molal volume at infinite dilution (\bar{V}_{conf}^0) or the molal volume holds accurately in the form:

$$\bar{V}_{\text{conf}}^0 = \bar{V}^0 - \kappa_T RT \quad (1)$$

$$= \alpha n + \beta, \quad (2)$$

where \bar{V}^0 , κ_T , R , T , and n denote the partial molal volume at infinite dilution (or the molal volume), the isothermal compressibility, the gas constant, the temperature, and the carbon number, respectively, and α and β are the parameters

independent of early on temper shows weak ar pressure. The v the demonstrati arises from the I In order to corr shed light on fa (2). None has a problem since t sufficient know structures were The compreh molecular point of the dimensions volume V_w of t purpose; here c involved. The a follows:

$$\bar{V}_{\text{conf}}^0 = (n - 2)$$

$$= (n - 2)$$

where \bar{V}^0 (—CF nions of the me ively, and α , β (—CH₂—) The most impo ntity rule is th groups constit (2) or (4). The measure how l the methylene er Waals volu to know the ex group differs fr and α_2 are infl calculated thes a model syst since the mole the crystal and named have th pective for ur different packi inner methylen by allowing fo and methylene

2. Linear Rel

2.1. Van der V

In this secti the constituent der Waals vol the van der V determined ex [3, 4]. Calcula mol⁻¹) of the